Supporting Information for

A Visible-Light-Induced Photocatalyst-Free Approach for C-3 Dicarbonyl Coumarins Production
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1. General information

All reactions were performed using quartz tube. Solvents were dried by standard methods before they were used. 3-Arylacetylene coumarins and 3-bromocoumarin were synthesized according to the literature.\textsuperscript{1,2,3} Commercial grade reagents were used without further purification. H$_2^{18}$O is purchased from Shanghai Yi Shi Chemical Co., purity 97%. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. All reactions were carried out with photoreactor (Serial No: PEA12) which was purchased from LUOYANG JINFENG ELECTROMECANICAL EQUIPMENT CO., LTD. The LCD Digital Hotplate Magnetic Stirrer MS-H-Pro$^+$ and Digital Single Channel Adjustable Automatic Electronic Pipette Micropipette dPettee$^+$ were purchased from Dragon Laboratory Instruments Limited. $^1$H NMR and $^{13}$C NMR spectra were recorded on 400 and 100 MHz NMR instruments using CDCl$_3$ as the solvent and TMS as the internal standard. $^{19}$F NMR spectra was recorded at 376.5 MHz on Bruker DPX-400, the chemical shifts $\delta$ are reported relative to CFCl$_3$ ($\delta$ = 0 ppm) as internal standard. The multiplicity of signals is designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd = doublet of doublet. High resolution mass spectra (HRMS) was obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionisation (ESI). The UV/Vis absorption spectra was recorded on a Perkin Elmer Lambda 35 Spectrometer and the fluorescence emission spectra were recorded using a F-4500 FL spectrophotometer. The X-ray single crystal structure was determined by the Oxford Diffraction Xcalibur CCD single crystal diffractometer. The illuminance of LED light was tested by the ZDS-10 digital luxmeter from Suzhou Tianwei Instrument Co., Ltd.

2. Experimental procedures

2.1 General procedure for synthesis of 3-arylacetylene coumarins from alkyne esters\textsuperscript{1}

To a reaction tube equipped with a magnetic stirring bar were added phenyl 3-phenylpropiolate (0.2 mmol), NIS (2 equiv.), MeCN (1.5 mL) stirred under 3 W blue LED ($E = 5.00-5.15 \times 10^4$ lx, $\lambda_{\text{max}} = 450-465$ nm) under air atmosphere and at room temperature for 24 hours. Then Pd(PPh$_3$)$_2$Cl$_2$ (0.0144 g, 10 mol%), CuI (0.0039 g, 10 mol%), phenylacetylene (3 equiv.) and Et$_3$N (0.5 mL) were added. The obtained reaction mixture was heated at 60 °C for 12 hours under Ar atmosphere. The solvent
was removed under vacuum, and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/dichloromethane = 6:1/3:1, v/v) to give the desired compound 1.

2.2 General procedure for the synthesis of 3-arylacetylene coumarins from 3-bromocoumarins

To a reaction tube equipped with a magnetic stirring bar were added 3-bromocoumarin (0.2 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.0144 g, 10 mol%), CuI (0.0039 g, 10 mol%), phenylacetylene (3 equiv.) and Et$_3$N (0.5 mL) were added. The obtained reaction mixture was heated at 60 °C for 12 hours under Ar atmosphere. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/dichloromethane = 6:1/3:1, v/v) to give the desired compound 1.

2.3 General procedure for the synthesis of C-3 dicarbonyl coumarins

To a reaction tube equipped with a magnetic stirring bar were added 3-arylacetylene coumarins (0.2 mmol), I$_2$ (2 equiv.), NaHCO$_3$ (3 equiv.), DCE:H$_2$O (2 mL, v/v = 200:3) stirred under 3 W blue LED (E = 5.00-5.15X10$^4$ lx, $\lambda_{max}$ = 450-465 nm) under oxygen atmosphere and at room temperature for 24 hours. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate/dichloromethane = 30:1/10:1:1, v/v) to give the desired compound 2.

3. Control experiments

In order to explore the possible mechanism of the present transformation, a series of control experiments were carried out (Scheme S2, exp 1-6). [2,2,6,6-tetramethylpiperidine]-1-oxyl (TEMPO) or butylated hydroxytoluene (BHT), a radical-trapping reagent was added into the reaction. When added 3-arylacetylene coumarin (0.2 mmol), I$_2$ (2 equiv.), NaHCO$_3$ (3 equiv.), TEMPO (126.3 mg, 0.8 mmol) (exp 1) or BHT (176.3 mg, 0.8 mmol) (exp 2) DCE:H$_2$O (2 mL, v/v = 200:3) stirred under 3 W blue LED (E = 5.00-5.15X10$^4$ lx, $\lambda_{max}$ = 450-465 nm) under oxygen atmosphere and at room temperature for 24 hours. The oxidation reaction was not completely inhibited. Meanwhile, five strong molecular ion peaks were obtained by ESI-MS and attributed to [I+H]$^+$ (exact mass: 590.9314), [I+H]$^+$ (exact mass: 590.9316), [II+H]$^+$ (exact mass: 369.1122), [III+H]$^+$ (exact mass: 158.1536) and [IV+H]$^+$ or [IV'+H]$^+$ (exact mass: 573.3001) (Fig. S1-S5).
**Scheme S2. Control experiments**

**Figure S1.** HRMS spectrum of compound [I+H]^+ for exp 1
Figure S2. HRMS spectrum of compound [II+H]^+ for exp 1

Figure S3. HRMS spectrum of compound [III+H]^+ for exp 1
4. H$_2^{18}$O isotopic labeling experiments

3-Arylacetylene coumarin (1a, 67.9 mg, 0.2 mmol), I$_2$ (104.7 mg, 2 equiv.), NaHCO$_3$ (50.4 mg, 3 equiv.), DCE:H$_2^{18}$O (2 mL, v/v = 200:3) stirred under 3 W blue LED (E = 5.00-5.15X$10^4$ lx, $\lambda_{max}$ = 450-465 nm) under argon atmosphere and at room temperature for 24 hours. After the reaction was
complete, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography and preparative TLC to afford the corresponding product, which was measured HRMS (Fig. S6).

\[
\begin{align*}
\text{exp 7: } & 2a - \text{momo}^{18}\text{O} : 2a - \text{di}^{18}\text{O} = 27\% : 43\% : 30\% \text{ (total conversion: } 40\%) \\
\end{align*}
\]

Scheme S3. \(H_2^{18}\text{O}\) isotopic labeling experiments under argon

Figure S6. HRMS spectrum of compound \([2a/2a-\text{momo}^{18}\text{O}/2a-\text{di}^{18}\text{O}+H]^+\) for exp 7

3-Arylacetylene coumarin (1a, 67.9 mg, 0.2 mmol), \(I_2\) (104.7 mg, 2 equiv.), \(\text{NaHCO}_3\) (50.4 mg, 3 equiv.), \(\text{DCE:}H_2^{18}\text{O}\) (2 mL, v/v = 200:3) stirred under 3 W blue LED (E = 5.00-5.15X10^4 lx, \(\lambda_{\text{max}}\) = 450-465 nm) under oxygen atmosphere and at room temperature for 24 hours. After the reaction was complete, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography and preparative TLC to afford the corresponding product, which was measured HRMS (Fig. S7-S8).
Scheme S4. H$_2^{18}$O isotopic labeling experiments

exp 8: 2a : 2a-mono$^{18}$O : 2a-di$^{18}$O = 94% : 6% : 0% (total conversion: 95%)

Figure S7. HRMS spectrum of compound [2a/2a-momo$^{18}$O+H]$^+$ for exp 8

Figure S8. HRMS spectrum of compound [2a-momo$^{18}$O+H]$^+$ for exp 8
5. UV/Vis absorption spectra of 3-arylacetylene coumarin precursors.

The UV/Vis absorption spectra was recorded in MeCN of a 0.05 mM solution in 10 mm path length quartz cuvette on a Perkin Elmer Lambda 35 Spectrometer.

**Table S1.** UV/Vis absorption spectra of 3-arylacetylene coumarin precursors in acetonitrile solutions.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1p</td>
<td>356</td>
</tr>
<tr>
<td>1q</td>
<td>347</td>
</tr>
<tr>
<td>1r</td>
<td>423</td>
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<tr>
<td>1s</td>
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</tr>
<tr>
<td>1aa</td>
<td>423</td>
</tr>
<tr>
<td>1ab</td>
<td>424</td>
</tr>
</tbody>
</table>

**Figure S9.** Absorption spectra of 1p-1u in MeCN
6. Fluorescent probe for hydrogen peroxide of 2r, 2z and 2ab

Probes 2r, 2z, 2ab were dissolved in DMF for a stock solution (1 mM). H$_2$O$_2$ was from dilution of 30% solution in water. Test solutions (10 μM) were prepared by displacing 30 μL of the stock solution into a 3 mL mixture of 0.01 M PBS and CH$_3$CN (8:2, v/v) at pH 7.4. The detection limit was calculated based on the fluorescence titration. Detection limit = 3σ/k. Where σ is the standard deviation of blank measurement, k is the slope between the fluorescence intensity ratio versus H$_2$O$_2$ concentration.

6.1 Fluorescent probe for hydrogen peroxide of 2r

Scheme S5. Fluorescent probe for hydrogen peroxide of 2r
The fluorescence emission spectrum of probe was 0.344621 by calculation. The k was 4.16472. Detection limit = deviation of blank measurement) was achieved. The data were acquired at 515 nm (n = 15).

Figure S11. (a) Changes in the absorption spectra of compound 2r in the presence of 100 equiv. of H₂O₂. (b) Time-dependent fluorescence spectral changes of compound 2r with 100 equiv. of H₂O₂ (λex = 360 nm, steady excitation). (c, d) Fluorescent emission spectra of compound 2r (10 μM) in the presence of 10-100 equiv. of H₂O₂ (Data were acquired at 515 nm)

The fluorescence emission spectrum of probe 2r was measured by 15 times and σ (the standard deviation of blank measurement) was achieved. The data were acquired at 515 nm (n = 15), and σ was 0.344621 by calculation. The k was 4.16472. Detection limit = 3σ/k = 0.2482 μM.

Figure S12. Intensity changes of 2r in fluorescence at 515 nm (λex= 360 nm) over time with or without H₂O₂
6.2 Fluorescent probe for hydrogen peroxide of 2z

![Scheme S6. Fluorescent probe for hydrogen peroxide of 2z](image)

**Figure S13.** (a) Changes in the absorption spectra of compound 2z in the presence of 100 equiv. of H₂O₂. (b) Time-dependent fluorescence spectral changes of compound 2z with 100 equiv. of H₂O₂ (λ_ex = 360 nm, steady excitation). (c, d) Fluorescent emission spectra of compound 2z (10 µM) in the presence of 10-100 equiv. of H₂O₂ (Data were acquired at 516 nm)

The fluorescence emission spectrum of probe 2z was measured by 15 times and σ (the standard deviation of blank measurement) was achieved. The data were acquired at 516 nm (n = 15), and σ was 0.295761 by calculation. The k was 2.47663. Detection limit = 3σ/k = 0.358 µM.
Figure S14. Intensity changes of 2z in fluorescence at 516 nm ($\lambda_{ex} = 360$ nm) over time with or without H$_2$O$_2$

6.3 Fluorescent probe for hydrogen peroxide of 2ab

Scheme S7. Fluorescent probe for hydrogen peroxide of 2ab

Figure S15. Fluorescent emission spectra of probe 2ab (10 μM) in the presence of 10-100 equiv. of H$_2$O$_2$. Data were acquired at 512 nm.

The fluorescence emission spectrum of probe 2ab was measured by 15 times and $\sigma$ (the standard deviation of blank measurement) was achieved. The data were acquired at 512 nm ($n = 15$), and $\sigma$ was 0.364074 by calculation. The $k$ was 7.29904. Detection limit = $3\sigma/k = 0.149$ μM.
Figure S16. Time-dependent fluorescence spectral changes of probe 2ab with 10 equiv. of 
\(\text{H}_2\text{O}_2\) (\(\lambda_{\text{ex}} = 360\) nm, steady excitation)

7. References


8. Characterization data

7-fluoro-4-phenyl-3-(p-tolylethynyl)-2H-chromen-2-one (1p)
Yellow solid (53.0 mg, 75%), mp. 204.9 - 207.3 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.61 - 7.52 (m, 3 H), 7.51 - 7.44 (m, 2 H), 7.30 - 7.23 (m, 1 H), 7.15 - 7.08 (m, 3 H), 7.07 - 7.01 (m, 2 H), 6.94 (td, $J$ = 2.5, 8.4 Hz, 1 H), 2.31 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 164.4 (d, $J$ = 255.3 Hz), 159.2, 155.2, 153.9 (d, $J$ = 13.2 Hz), 139.2, 134.3, 131.6, 129.5, 129.3 (d, $J$ = 10.3 Hz), 129.1, 129.0, 128.5, 119.3, 116.6 (d, $J$ = 2.9 Hz), 112.6 (d, $J$ = 22.7), 110.3 (d, $J$ = 2.9 Hz), 104.5 (d, $J$ = 25.7 Hz), 99.1, 82.9, 21.6. $^{19}$F NMR (376.5 MHz, CDCl$_3$): $\delta$ -104.8. HRMS (ESI) calcd. for C$_{24}$H$_{15}$FO$_2$ (M+H)$^+$: 355.1129, found: 355.1128.

7-methyl-3-(phenylethynyl)-2H-chromen-2-one (1q)
White solid (38.1 mg, 73%). mp. 166.6 - 169.2 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.91 (s, 1 H), 7.57 (dd, $J$ = 3.0, 6.5 Hz, 2 H), 7.40 - 7.32 (m, 4 H), 7.16 - 7.08 (m, 2 H), 2.46 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.6, 153.5, 144.8, 143.7, 131.9, 129.0, 128.4, 127.4, 126.1, 122.4, 117.0, 116.6, 111.8, 95.3, 83.5, 21.9. HRMS (ESI) calcd. for C$_{18}$H$_{12}$O$_2$ (M+H)$^+$: 261.0910, found: 261.0909.

7-(diethylamino)-3-(phenylethynyl)-2H-chromen-2-one (1r)
Yellow solid (59.1 mg, 92%), mp. 145.7 - 148.6 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79 (s, 1 H), 7.58 - 7.51 (m, 2 H), 7.36 - 7.30 (m, 3 H), 7.27 - 7.22 (m, 1 H), 6.58 (dd, $J$ = 2.4, 8.9 Hz, 1 H), 6.49 (d, $J$ = 2.3 Hz, 1 H), 3.42 (q, $J$ = 7.1 Hz, 4 H), 1.22 (t, $J$ = 7.1 Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$):
δ 161.0, 156.3, 151.1, 145.5, 131.7, 128.9, 128.4, 128.3, 123.1, 109.2, 108.4, 104.7, 97.3, 93.3, 84.6, 45.0, 12.5. HRMS (ESI) calcd. for C_{21}H_{19}NO_{2} (M+H)^+: 318.1489, found: 318.1488.

3-(phenylethynyl)-2H-chromen-2-one (1s)
Light yellow solid (30.6 mg, 62%), mp. 174.6 - 176.9 °C. ^1^H NMR (400 MHz, CDCl$_3$): δ 7.95 (s, 1 H), 7.63 - 7.46 (m, 4 H), 7.40 - 7.27 (m, 5 H). ^1^C NMR (100 MHz, CDCl$_3$): δ 159.3, 153.3, 144.7, 132.1, 132.0, 129.1, 128.4, 127.7, 124.8, 122.2, 118.9, 116.8, 113.1, 95.8, 83.3. HRMS (ESI) calcd. for C$_{17}$H$_{10}$O$_2$ (M+H)$^+$: 247.0754, found: 247.0755.

3-(p-tolylethynyl)-2H-chromen-2-one (1t)
Yellow solid (36.3 mg, 70%), mp. 132.3 - 135.7 °C. ^1^H NMR (400 MHz, CDCl$_3$): δ 7.92 (s, 1 H), 7.56 - 7.43 (m, 4 H), 7.36 - 7.25 (m, 2 H), 7.16 (d, $J = 7.9$ Hz, 2 H), 2.37 (s, 3 H). ^1^C NMR (100 MHz, CDCl$_3$): δ 159.4, 153.2, 144.4, 139.5, 132.0, 131.9, 129.2, 127.7, 124.8, 119.1, 119.0, 116.8, 113.2, 96.2, 82.8, 21.6. HRMS (ESI) calcd. for C$_{18}$H$_{12}$O$_2$ (M+H)$^+$: 261.0910, found: 261.0912.

3-((4-methoxyphenyl)ethynyl)-2H-chromen-2-one (1u)
Yellow solid (33.1 mg, 60%), mp. 162.1 - 164.9 °C. ^1^H NMR (400 MHz, CDCl$_3$): δ 7.90 (s, 1 H), 7.55 - 7.46 (m, 4 H), 7.37 - 7.27 (m, 2 H), 6.88 (d, $J = 8.8$ Hz, 2 H), 3.83 (s, 3 H). ^1^C NMR (100 MHz, CDCl$_3$): δ 160.3, 159.4, 153.2, 144.0, 133.6, 131.9, 127.6, 124.8, 119.0, 116.8, 114.3, 114.1, 113.4, 96.2, 82.3, 55.3. HRMS (ESI) calcd. for C$_{18}$H$_{12}$O$_3$ (M+H)$^+$: 277.0859, found: 277.0856.
3-((4-fluorophenyl)ethynyl)-2H-chromen-2-one (1v)
White solid (37.9 mg, 77%), mp. 61.5 - 61.8 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.94 (s, 1 H), 7.64 - 7.45 (m, 4 H), 7.40 - 7.27 (m, 2 H), 7.12 - 7.01 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 163.0 (d, $J$ = 250.9 Hz ), 159.3, 153.3, 144.7, 134.0 (d, $J$ = 8.8 Hz ), 132.2, 127.7, 124.9, 118.9, 118.3 (d, $J$ = 2.9 Hz ), 116.8, 115.9 (d, $J$ = 22.0 Hz ), 113.0, 94.7, 83.1. HRMS (ESI) calcd. for C$_{17}$H$_9$FO$_2$ (M+H)$^+$: 265.0659, found: 265.0656.

3-((2-methoxyphenyl)ethynyl)-2H-chromen-2-one (1w)
Yellow solid (29.0 mg, 53%), mp. 107.3 - 109.6 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.96 (s, 1 H), 7.58 - 7.45 (m, 3 H), 7.38 - 7.25 (m, 3 H), 6.98 - 6.89 (m, 2 H), 3.93 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 160.3, 159.4, 153.3, 144.4, 134.0, 132.0, 130.8, 127.7, 124.8, 120.5, 119.0, 116.8, 113.4, 111.4, 110.7, 92.5, 87.3, 55.9. HRMS (ESI) calcd. for C$_{18}$H$_{12}$O$_3$ (M+H)$^+$: 277.0859, found: 277.0861.

3-((4-(trifluoromethyl)phenyl)ethynyl)-2H-chromen-2-one (1x)
Yellow solid (48.5 mg, 77%), mp. 140.3 - 142.8 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.00 (s, 1 H), 7.71 - 7.66 (m, J = 8.2 Hz, 2 H), 7.65 - 7.60 (m, J = 8.4 Hz, 2 H), 7.57 (td, J = 1.6, 7.8 Hz, 1 H), 7.51 (dd, J = 1.4, 7.8 Hz, 1 H), 7.39 - 7.29 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 159.1, 153.5, 145.6, 132.6, 132.2, 130.7 (q, J = 33.0 Hz), 127.9, 126.0 (d, J = 1.47 Hz), 125.4 (q, J = 3.7 Hz), 125.0, 123.8 (d, J = 272.2 Hz), 118.7, 116.9, 112.5, 94.0, 85.5. $^{19}$F NMR (376.5 MHz, CDCl$_3$): δ -62.9. HRMS (ESI) calcd. for C$_{18}$H$_9$F$_3$O$_2$ (M+H)$^+$: 315.0627, found: 315.0627.
7-(diethylamino)-3-((p-tolylethynyl)-2H-chromen-2-one (1y)

Yellow solid (58.6 mg, 88%), mp. 182.5 - 184.7 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.77 (s, 1 H), 7.47 - 7.41 (m, $J$ = 8.1 Hz, 2 H), 7.24 (d, $J$ = 8.8 Hz, 1 H), 7.17 - 7.10 (m, $J$ = 7.9 Hz, 2 H), 6.58 (dd, $J$ = 2.4, 8.9 Hz, 1 H), 6.52 - 6.45 (m, 1 H), 3.42 (q, $J$ = 7.1 Hz, 4 H), 2.36 (s, 3 H), 1.22 (t, $J$ = 7.1 Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.0, 156.2, 151.0, 145.2, 138.5, 131.6, 129.0, 128.8, 120.0, 109.2, 108.5, 105.0, 97.3, 93.5, 83.9, 44.9, 21.5, 12.5. HRMS (ESI) calcd. for C$_{22}$H$_{21}$NO$_2$ (M+H)$^+$: 332.1645, found: 332.1645.

7-(diethylamino)-3-((4-methoxyphenyl)ethynyl)-2H-chromen-2-one (1z)

Yellow solid (59.6 mg, 85%), mp. 135.1 - 137.6 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75 (s, 1 H), 7.51 - 7.45 (m, 2 H), 7.23 (d, $J$ = 8.8 Hz, 1 H), 6.88 - 6.83 (m, 2 H), 6.57 (dd, $J$ = 2.5, 8.9 Hz, 1 H), 6.47 (d, $J$ = 2.3 Hz, 1 H), 3.82 (s, 3 H), 3.41 (q, $J$ = 7.1 Hz, 4 H), 1.21 (t, $J$ = 7.1 Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.1, 159.7, 156.1, 150.9, 145.0, 133.2, 128.8, 115.2, 113.9, 109.2, 108.5, 105.0, 97.3, 93.4, 83.3, 55.3, 44.9, 12.5. HRMS (ESI) calcd. for C$_{22}$H$_{21}$NO$_3$ (M+H)$^+$: 348.1594, found: 348.1598.

7-(diethylamino)-3-((4-fluorophenyl)ethynyl)-2H-chromen-2-one (1aa)

7-(diethylamino)-3-((4-fluorophenyl)ethynyl)-2H-chromen-2-one (1aa)
Yellow solid (61.8 mg, 92%), mp. 163.7 - 165.6 °C. 1H NMR (400 MHz, CDCl3): δ 7.78 (s, 1 H), 7.56 - 7.49 (m, 2 H), 7.24 (s, 1 H), 7.02 (t, J = 8.7 Hz, 2 H), 6.59 (dd, J = 2.3, 8.8 Hz, 1 H), 6.49 (s, 1 H), 3.43 (d, J = 7.1 Hz, 4 H), 1.22 (t, J = 7.2 Hz, 6 H).

13C NMR (100 MHz, CDCl3): δ 162.6 (d, J = 249.2 Hz), 160.9, 156.3, 151.1, 145.5, 133.6, 128.9, 119.2 (d, J = 3.67 Hz), 115.6 (d, J = 22.0 Hz), 109.3, 108.4, 104.5, 97.4, 92.2, 84.3, 45.0, 12.5. 19F NMR (376.5 MHz, CDCl3): δ -110.73. HRMS (ESI) calcd. for C21H18FNO2 (M+H)+: 336.1394, found: 336.1394.

O

N

CF3

7-(diethylamino)-3-((4-(trifluoromethyl)phenyl)ethynyl)-2H-chromen-2-one (1ab)
White solid (68.9 mg, 89%), mp. 184.7 - 186.4 °C. 1H NMR (400 MHz, CDCl3): δ 7.83 (s, 1 H), 7.66 - 7.61 (m, J = 8.1 Hz, 2 H), 7.61 - 7.56 (m, J = 8.6 Hz, 2 H), 7.29 - 7.24 (m, 1 H), 6.60 (dd, J = 2.4, 8.9 Hz, 1 H), 6.49 (d, J = 2.3 Hz, 1 H), 3.43 (q, J = 7.1 Hz, 4 H), 1.23 (t, J = 7.1 Hz, 6 H). 13C NMR (100 MHz, CDCl3): δ 160.8, 156.5, 151.4, 146.3, 131.8, 129.8 (q, J = 33.0 Hz), 129.2, 126.9 (d, J = 1.5 Hz), 124.0 (q, J = 272.2 Hz), 125.2 (q, J = 3.7 Hz), 109.4, 108.3, 103.8, 97.3, 91.8, 87.2, 45.0, 12.5. 19F NMR (376.5 MHz, CDCl3): δ -62.8. HRMS (ESI) calcd. for C22H18F3NO3 (M+H)+: 386.1362, found: 386.1362.

O

Me

1-(7-methyl-2-oxo-4-phenyl-2H-chromen-3-yl)-2-phenylethane-1,2-dione (2a)
Yellow solid (64.0 mg, 87%), mp. 150.1 - 151.7 °C. 1H NMR (400 MHz, CDCl3): δ 7.96 (d, J = 7.5 Hz, 2 H), 7.62 - 7.53 (m, 1 H), 7.50 - 7.35 (m, 7 H), 7.28 - 7.22 (m, 1 H), 7.18 (d, J = 8.2 Hz, 1 H), 7.06 (d, J = 8.1 Hz, 1 H), 2.47 (s, 3 H). 13C NMR (100 MHz, CDCl3): δ 191.3, 190.7, 159.8, 158.9, 154.3, 145.9, 134.2, 132.5, 132.0, 130.4, 130.4, 129.6, 128.8, 128.7, 128.5, 128.3, 126.3, 121.8, 117.5, 117.3, 21.9. HRMS (ESI) calcd. for C24H16O4 (M+H)+: 369.1121, found: 369.1123.
1-(7-(tert-butyl)-2-oxo-4-phenyl-2H-chromen-3-yl)-2-phenylethane-1,2-dione (2b)
Yellow solid (62.0 mg, 76%), mp. 173.7 - 175.3 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.00 - 7.92 (m, 2 H), 7.59 (t, $J$ = 7.5 Hz, 1 H), 7.49 - 7.42 (m, 6 H), 7.42 - 7.37 (m, 2 H), 7.33 - 7.27 (m, 1 H), 7.25 (d, $J$ = 8.4 Hz, 1 H), 1.35 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.3, 190.7, 160.0, 159.0, 158.8, 154.3, 134.2, 132.5, 132.0, 130.4, 129.6, 128.7, 128.7, 128.5, 128.2, 122.6, 122.0, 117.2, 114.1, 35.5, 30.9. HRMS (ESI) calcd. for C$_{27}$H$_{22}$O$_4$ (M+H)$^+$: 394.2013, found: 394.2015.

1-(2-oxo-4-phenyl-2H-chromen-3-yl)-2-phenylethane-1,2-dione (2c)
Yellow solid (52.5 mg, 74%), mp. 178.1 - 180.9 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.02 - 7.94 (m, 2 H), 7.69 - 7.55 (m, 2 H), 7.52 - 7.38 (m, 8 H), 7.36 - 7.31 (m, 1 H), 7.30 - 7.23 (m, 1 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.0, 190.4, 159.5, 158.5, 154.1, 134.3, 133.9, 132.2, 131.8, 130.5, 129.7, 129.1, 128.7, 128.6, 128.3, 125.0, 123.2, 119.6, 117.3. HRMS (ESI) calcd. for C$_{23}$H$_{14}$O$_4$ (M+H)$^+$: 355.0965, found: 355.0967.

1-(7-fluoro-2-oxo-4-phenyl-2H-chromen-3-yl)-2-phenylethane-1,2-dione (2d)
Yellow solid (49.2 mg, 66%), mp. 165.8 - 167.4 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.99 - 7.93 (m, 2 H), 7.64 - 7.56 (m, 1 H), 7.51 - 7.42 (m, 5 H), 7.41 - 7.36 (m, 2 H), 7.33 (dd, $J$ = 6.1, 8.9 Hz, 1 H), 7.16 (dd, $J$ = 2.3, 8.7 Hz, 1 H), 7.00 (td, $J$ = 2.4, 8.4 Hz, 1 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.7, 190.4, 165.7 (d, $J$ = 258.23 Hz ), 159.2, 158.1, 155.4 (d, $J$ = 13.2 Hz ), 134.4, 132.1, 131.8, 131.1 (d, $J$ = 10.3 Hz ), 130.4, 129.9, 129.8, 128.6, 128.2, 122.2 (d, $J$ = 2.9 Hz ), 116.5 (d, $J$ = 2.9 Hz ), 113.3 (d, $J$ = 22.7 Hz ), 104.9 (d, $J$ = 25.7 Hz ). $^{19}$F NMR (376.5 MHz, CDCl$_3$): $\delta$ -101.2. HRMS (ESI) calcd. for C$_{23}$H$_{13}$FO$_4$ (M+Na)$^{+}$: 395.0690, found: 395.0693.
1-(7-chloro-2-oxo-4-phenyl-2H-chromen-3-yl)-2-phenylethane-1,2-dione (2e)
Yellow solid (54.3 mg, 70%). mp. 225.8 - 227.5 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.00 - 7.91 (m, 2 H), 7.63 - 7.56 (m, 1 H), 7.50 - 7.42 (m, 6 H), 7.41 - 7.34 (m, 2 H), 7.29 - 7.20 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.6, 190.3, 158.9, 157.8, 154.3, 140.1, 134.4, 131.9, 131.7, 130.5, 129.9, 128.9, 128.6, 128.2, 125.6, 123.1, 118.3, 117.6. HRMS (ESI) calcd. for C$_{23}$H$_{13}$ClO$_4$ (M+Na)$^+$: 411.0395, found: 411.0396.

1-(2-oxo-4-phenyl-7-(trifluoromethyl)-2H-chromen-3-yl)-2-phenylethane-1,2-dione (2f)
Yellow solid (45.5 mg, 54%), mp. 148.1 - 149.7 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.02 - 7.94 (m, 2 H), 7.71 (s, 1 H), 7.65 - 7.57 (m, 1 H), 7.53 - 7.44 (m, 8 H), 7.41 (dd, $J$ = 3.0, 6.7 Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.1, 189.9, 158.6, 156.7, 153.6, 135.0 (q, $J$ = 33.8 Hz), 134.6, 131.6, 131.4, 130.5, 130.1, 129.8, 129.0, 128.6, 128.3, 125.4, 122.9 (q, $J$ = 272.9 Hz), 122.2, 121.4 (q, $J$ = 3.67 Hz), 114.8 (q, $J$ = 3.7 Hz). $^{19}$F NMR (376.5 MHz, CDCl$_3$): $\delta$ -63.14. HRMS (ESI) calcd. for C$_{24}$H$_{13}$F$_3$O$_4$ (M+H)$^+$: 423.0839, found: 423.0838.

1-(6,8-dimethyl-2-oxo-4-phenyl-2H-chromen-3-yl)-2-phenylethane-1,2-dione (2g)
Yellow solid (67.1 mg, 88%), mp. 152.9 - 155.8 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.96 (d, $J$ = 7.5 Hz, 2 H), 7.61 - 7.53 (m, 1 H), 7.50 - 7.41 (m, 5 H), 7.41 - 7.35 (m, 2 H), 7.30 (s, 1 H), 6.89 (s, 1 H), 2.45 (s, 3 H), 2.26 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.3, 190.6, 159.8, 158.9, 150.7, 136.5,
134.2, 134.1, 132.7, 132.0, 129.5, 128.6, 128.5, 128.3, 126.5, 126.4, 122.6, 119.2, 20.9, 15.5. HRMS (ESI) calcd. for C_{25}H_{18}O_4 (M+Na)^+: 405.1097, found: 405.1098.

1-(7-methyl-2-oxo-4-phenyl-2H-chromen-3-yl)-2-(p-tolyl)ethane-1,2-dione (2h)
Yellow solid (64.8 mg, 85%), mp. 63.3 - 65.1 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.87 (d, J = 8.2 Hz, 2 H), 7.49 - 7.43 (m, 3 H), 7.41 - 7.36 (m, 2 H), 7.25 (d, J = 8.6 Hz, 3 H), 7.18 (d, J = 8.2 Hz, 1 H), 7.06 (dd, J = 1.0, 8.2 Hz, 1 H), 2.47 (s, 3 H), 2.40 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 191.4, 190.3, 159.8, 158.7, 154.2, 145.8, 145.4, 132.6, 130.5, 129.6, 129.5, 129.3, 128.8, 128.7, 128.3, 126.2, 122.0, 117.4, 117.3, 21.9. HRMS (ESI) calcd. for C_{25}H_{18}O_4 (M+Na)^+: 405.1097, found: 405.1099.

1-(4-methoxyphenyl)-2-(7-methyl-2-oxo-4-phenyl-2H-chromen-3-yl)ethane-1,2-dione (2i)
Yellow oil (65.5 mg, 82%). ¹H NMR (400 MHz, CDCl₃): δ 7.99 - 7.92 (m, 2 H), 7.48 - 7.42 (m, 3 H), 7.42 - 7.35 (m, 2 H), 7.23 (s, 1 H), 7.18 (d, J = 8.2 Hz, 1 H), 7.09 - 7.01 (m, 1 H), 6.95 - 6.87 (m, 2 H), 3.86 (s, 3 H), 2.47 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 191.5, 189.2, 164.5, 159.7, 158.4, 154.2, 145.7, 132.9, 132.6, 129.5, 128.7, 128.6, 128.3, 126.2, 124.9, 122.3, 117.4, 117.3, 114.0, 55.6, 21.9. HRMS (ESI) calcd. for C_{25}H_{18}O_5 (M+Na)^+: 421.1046, found: 421.1047.

1-(4-fluorophenyl)-2-(7-methyl-2-oxo-4-phenyl-2H-chromen-3-yl)ethane-1,2-dione (2j)
Yellow solid (61.7 mg, 80%), mp. 126.4 - 128.2 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.04 - 7.97 (m, 2 H), 7.50 - 7.43 (m, 3 H), 7.41 - 7.36 (m, 2 H), 7.26 (d, J = 3.2 Hz, 1 H), 7.20 (d, J = 8.2 Hz, 1 H), 7.16 - 7.05 (m, 3 H), 2.49 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 191.2, 189.1, 166.5 (d, J = 256.8 Hz), 159.9, 159.0, 154.3, 146.0, 133.2 (d, J = 9.5 Hz), 132.4, 129.7, 128.9, 128.7, 128.4 (d, J = 2.9
(d, J = 22.0 Hz), 117.9, 117.3, 115.8 (d, J = 22.0 Hz), 21.9. \textsuperscript{19}F NMR (376.5 MHz, CDCl\textsubscript{3}): δ -120.6. HRMS (ESI) calcd. for C\textsubscript{24}H\textsubscript{15}FO\textsubscript{4} (M+Na): 409.0847, found: 409.0849.

\begin{center}
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\end{center}

\textbf{1-(2-methoxyphenyl)-2-(7-methyl-2-oxo-4-phenyl-2\textit{H}-chromen-3-yl)ethane-1,2-dione (2l)}

Yellow solid (51.5 mg, 65%). mp. 147.3 - 149.5 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.93 (dd, J = 1.7, 7.8 Hz, 1 H), 7.55 - 7.45 (m, 4 H), 7.36 - 7.29 (m, 2 H), 7.23 (s, 1 H), 7.16 - 7.11 (m, 1 H), 7.07 - 7.01 (m, 2 H), 6.93 (d, J = 8.4 Hz, 1 H), 3.74 (s, 3 H), 2.47 (s, 3 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 190.8, 189.4, 160.8, 160.3, 159.9, 154.5, 146.2, 135.7, 133.3, 131.0, 129.3, 129.1, 128.5, 127.8, 126.1, 122.9, 121.1, 118.8, 117.9, 117.3, 112.5, 56.2, 21.9. HRMS (ESI) calcd. for C\textsubscript{25}H\textsubscript{18}O\textsubscript{5} (M+H): 399.1127, found: 399.1129.

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\end{center}

\textbf{1-(2-fluorophenyl)-2-(7-methyl-2-oxo-4-phenyl-2\textit{H}-chromen-3-yl)ethane-1,2-dione (2m)}

White solid (30.7 mg, 41%), mp. 178.3 - 180.2 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.02 - 7.93 (m, 1 H), 7.63 - 7.54 (m, 1 H), 7.53 - 7.45 (m, 3 H), 7.36 (dd, J = 2.8, 6.4 Hz, 2 H), 7.29 - 7.24 (m, 3 H), 7.18 (d, J = 8.3 Hz, 1 H), 7.14 - 7.04 (m, 2 H), 2.49 (s, 3 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 189.8, 188.5, 162.8 (d, J = 258.9 Hz), 161.0, 160.3, 154.5, 146.5, 136.0 (d, J = 9.5 Hz), 132.8, 131.2 (d, J = 1.5 Hz), 129.4, 129.3, 128.6, 127.9, 126.3, 124.4 (d, J = 3.7 Hz), 121.4 (d, J = 11.0 Hz), 119.2, 117.7, 117.4, 116.5 (d, J = 22.0 Hz), 22.0. \textsuperscript{19}F NMR (376.5 MHz, CDCl\textsubscript{3}): δ -106.7. HRMS (ESI) calcd. for C\textsubscript{24}H\textsubscript{15}FO\textsubscript{4} (M+Na): 409.0847, found: 409.0845.

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\includegraphics[width=0.5\textwidth]{structure3.png}
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\textbf{1-(7-methoxy-2-oxo-4-phenyl-2\textit{H}-chromen-3-yl)-2-(4-methoxyphenyl)ethane-1,2-dione (2n)}

Yellow oil (68.6 mg, 55%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.93 (d, J = 8.7 Hz, 2 H), 7.43 (s, 3 H), 7.40 - 7.33 (m, 2 H), 7.19 (d, J = 8.8 Hz, 1 H), 6.95 - 6.85 (m, 3 H), 6.79 (dd, J = 2.3, 9.0 Hz, 1 H),
3.88 (s, 3 H), 3.85 (s, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 191.7, 189.5, 164.6, 164.5, 159.9, 159.1, 156.3, 132.9, 132.8, 130.3, 129.5, 128.6, 128.2, 125.0, 119.7, 113.9, 113.5, 113.3, 100.9, 56.1, 55.6. HRMS (ESI) calcd. for C\(_{25}\)H\(_{18}\)O\(_6\) (M+Na): 437.0996, found: 437.0998.

1-(7-(tert-butyl)-2-oxo-4-phenyl-2\(H\)-chromen-3-yl)-2-(4-fluorophenyl)ethane-1,2-dione (2o)
Yellow solid (68.6 mg, 80%). mp. 144.9 - 147.3 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.04 - 7.97 (m, 2 H), 7.50 - 7.43 (m, 4 H), 7.39 (dd, \(J\) = 3.0, 6.8 Hz, 2 H), 7.34 - 7.28 (m, 1 H), 7.27 - 7.23 (m, 1 H), 7.17 - 7.09 (m, 2 H), 1.36 (s, 9 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 191.1, 189.1, 166.4 (d, \(J\) = 256.8 Hz), 160.0, 159.1, 158.9, 154.3, 133.2 (d, \(J\) = 9.5 Hz), 132.5, 129.6, 128.7, 128.6, 128.4 (d, \(J\) = 2.9 Hz), 128.2, 122.7, 121.9, 117.2, 115.8 (d, \(J\) = 22.0 Hz), 114.2, 35.5, 30.9. \(^{19}\)F NMR (376.5 MHz, CDCl\(_3\)): \(\delta\) -102.7. HRMS (ESI) calcd. for C\(_{27}\)H\(_{21}\)FO\(_4\) (M+H): 429.1497, found: 429.1493.

1-(7-fluoro-2-oxo-4-phenyl-2\(H\)-chromen-3-yl)-2-(p-tolyl)ethane-1,2-dione (2p)
Yellow solid (68.9 mg, 89%), mp. 144.3 - 146.1 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.86 (d, \(J\) = 8.3 Hz, 2 H), 7.49 - 7.43 (m, 3 H), 7.42 - 7.36 (m, 2 H), 7.32 (dd, \(J\) = 6.0, 8.8 Hz, 1 H), 7.25 (d, \(J\) = 7.8 Hz, 2 H), 7.15 (dd, \(J\) = 2.5, 8.5 Hz, 1 H), 7.03 - 6.96 (m, 1 H), 2.41 (s, 3 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 190.8, 190.0, 165.6 (d, \(J\) = 258.2 Hz), 159.1, 157.8, 155.4 (d, \(J\) = 13.2 Hz), 145.6, 132.2, 131.0 (d, \(J\) = 10.3 Hz), 130.6, 129.8, 129.4, 129.3, 128.8, 128.2, 122.3 (d, \(J\) = 2.9 Hz), 116.5 (d, \(J\) = 2.9 Hz), 113.2 (d, \(J\) = 22.0 Hz), 104.8 (d, \(J\) = 25.7 Hz), 21.9. \(^{19}\)F NMR (376.5 MHz, CDCl\(_3\)): \(\delta\) -101.5. HRMS (ESI) calcd. for C\(_{24}\)H\(_{13}\)FO\(_4\) (M+H): 387.1027, found: 387.1029.

1-(7-methyl-2-oxo-2\(H\)-chromen-3-yl)-2-phenylethane-1,2-dione (2q)
Yellow solid (54.3 mg, 93%), mp. 175.6 - 177.3 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.64 (s, 1 H), 7.99 - 7.92 (m, 2 H), 7.67 - 7.58 (m, 2 H), 7.55 - 7.46 (m, 2 H), 7.23 - 7.18 (m, 2 H), 2.51 (s, 3 H).
**1-(7-(sec-butyl)-2-oxo-2H-chromen-3-yl)-2-phenylethane-1,2-dione (2r)**

Yellow solid (43.3 mg, 62%), mp. 192.4 - 194.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.53 (s, 1 H), 7.98 - 7.90 (m, 2 H), 7.59 (d, J = 7.5 Hz, 1 H), 7.46 (d, J = 9.0 Hz, 2 H), 7.50 (d, J = 7.8 Hz, 1 H), 6.66 (dd, J = 2.4, 9.0 Hz, 1 H), 6.47 (d, J = 2.3 Hz, 1 H), 3.48 (q, J = 7.2 Hz, 4 H), 1.26 (t, J = 7.2 Hz, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ 194.0, 192.2, 160.6, 159.4, 154.0, 148.3, 134.0, 133.0, 132.7, 129.5, 128.8, 112.9, 110.4, 108.6, 97.1, 45.4, 12.5. HRMS (ESI) calcd. for C₂₁H₁₉NO₄ (M+H)⁺: 350.1387, found: 350.1390.

**1-(2-oxo-2H-chromen-3-yl)-2-phenylethane-1,2-dione (2s)**

Yellow solid (44.0 mg, 79%), mp. 152.1 - 154.3 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.66 (s, 1 H), 8.00 - 7.93 (m, 2 H), 7.75 - 7.62 (m, 3 H), 7.56 - 7.48 (m, 2 H), 7.43 - 7.35 (m, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ 192.2, 191.3, 159.0, 155.7, 148.8, 135.4, 134.5, 132.3, 130.7, 129.8, 128.9, 125.4, 122.5, 118.2, 117.2. HRMS (ESI) calcd. for C₁₇H₁₀O₄ (M+H)⁺: 279.0652, found: 279.0649.

**1-(2-oxo-2H-chromen-3-yl)-2-(p-tolyl)ethane-1,2-dione (2t)**

Light yellow (49.8 mg, 85%), mp. 183.4 - 185.7 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.65 (s, 1 H), 7.90 - 7.83 (m, J = 8.2 Hz, 2 H), 7.76 - 7.67 (m, 2 H), 7.43 - 7.36 (m, 2 H), 7.35 - 7.29 (m, J = 7.9 Hz, 2 H), 2.44 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 191.9, 191.4, 158.9, 155.7, 148.7, 145.8, 135.3, 130.6, 130.0, 129.8, 129.7, 125.4, 122.7, 118.2, 117.2, 22.0. HRMS (ESI) calcd. for C₁₈H₁₂O₄ (M+H)⁺: 293.0808, found: 293.0808.
1-(4-methoxyphenyl)-2-(2-oxo-2H-chromen-3-yl)ethane-1,2-dione (2u)
Yellow solid (52.4 mg, 85%), mp. 166.7 - 168.2 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.63 (s, 1 H), 7.98 - 7.92 (m, 2 H), 7.73-7.67 (m, 2 H), 7.41 - 7.35 (m, 2 H), 7.02 - 6.93 (m, 2 H), 3.89 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 191.3, 190.7, 164.8, 158.8, 155.7, 148.6, 135.2, 132.3, 130.5, 125.3, 125.3, 122.9, 118.2, 117.2, 114.4, 55.6. HRMS (ESI) calcd. for C$_{18}$H$_{12}$O$_5$ (M+H)$^+$: 309.0757, found: 309.0756.

1-(4-fluorophenyl)-2-(2-oxo-2H-chromen-3-yl)ethane-1,2-dione (2v)
Light yellow (53.6 mg, 91%), mp. 180.9 - 182.3 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.65 (s, 1 H), 8.05 - 7.96 (m, 2 H), 7.78 - 7.67 (m, 2 H), 7.46 - 7.37 (m, 2 H), 7.20 (t, J = 8.7 Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 191.0, 190.5, 166.6 (d, J = 257.5 Hz ), 159.0, 155.7, 148.9, 135.5, 132.5 (d, J = 10.27 Hz ), 130.7, 128.7 (d, J = 2.9 Hz ), 125.5, 122.6, 118.1, 117.3, 116.3 (d, J = 22.0Hz ). $^{19}$F NMR (376.5 MHz, CDCl$_3$): δ -102.0. HRMS (ESI) calcd. for C$_{17}$H$_9$FO$_4$ (M+H)$^+$: 297.0558, found: 297.0555.

1-(2-methoxyphenyl)-2-(2-oxo-2H-chromen-3-yl)ethane-1,2-dione (2w)
Light yellow (26.3 mg, 43%), mp. 187.6 - 189.9 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.72 (s, 1 H), 8.08 (dd, J = 1.7, 7.8 Hz, 1 H), 7.76 - 7.66 (m, 2 H), 7.63 - 7.56 (m, 1 H), 7.43 - 7.35 (m, 2 H), 7.18 - 7.10 (m, 1 H), 6.97 (d, J = 8.3 Hz, 1 H), 3.71 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 191.8, 189.1, 160.5, 159.0, 155.6, 147.9, 136.3, 135.0, 130.5, 130.4, 125.3, 122.9, 121.8, 121.7, 118.3, 117.1, 112.4, 56.0. HRMS (ESI) calcd. for C$_{18}$H$_{12}$O$_5$ (M+H)$^+$: 309.0757, found: 309.0760.
1-(2-oxo-2H-chromen-3-yl)-2-(4-(trifluoromethyl)phenyl)ethane-1,2-dione (2x)

Yellow solid (53.5 mg, 77%), mp. 196.1 - 197.2 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.68 (s, 1 H), 8.08 (d, $J$ = 8.2 Hz, 2 H), 7.82 - 7.71 (m, 4 H), 7.45 - 7.38 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.1, 190.8, 159.3, 155.7, 149.0, 135.7, 135.5 (d, $J$ = 33.01 Hz), 135.0, 130.8, 130.0, 126.0 (q, $J$ = 3.7 Hz), 125.6, 123.5 (q, $J$ = 272.9 Hz), 122.3, 118.1, 117.3. $^{19}$F NMR (376.5 MHz, CDCl$_3$): $\delta$ -63.3. HRMS (ESI) calcd. for C$_{18}$H$_{9}$F$_3$O$_4$ (M+H)$^+$: 347.0526, found: 347.0526.

1-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-2-(p-tolyl)ethane-1,2-dione (2y)

Yellow solid (44.3 mg, 61%), mp. 180.3 - 182.1 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.51 (s, 1 H), 7.83 (d, $J$ = 8.2 Hz, 2 H), 7.44 (d, $J$ = 9.0 Hz, 1 H), 7.28 (d, $J$ = 7.9 Hz, 2 H), 6.65 (dd, $J$ = 2.4, 9.0 Hz, 1 H), 6.46 (d, $J$ = 2.2 Hz, 1 H), 3.47 (q, $J$ = 7.1 Hz, 4 H), 2.41 (s, 3 H), 1.25 (t, $J$ = 7.2 Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 193.7, 192.3, 160.4, 159.3, 153.9, 148.3, 145.0, 132.6, 130.6, 129.6, 129.5, 113.1, 110.3, 108.5, 97.1, 45.3, 21.9, 12.5. HRMS (ESI) calcd. for C$_{22}$H$_{21}$NO$_4$ (M+Na)$^+$: 386.1363, found: 386.1362.

1-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-2-(p-tolyl)ethane-1,2-dione (2z)

Yellow solid (50.6 mg, 67%), mp. 187.5 - 189.7 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.51 (s, 1 H), 7.94 - 7.89 (m, 2 H), 7.44 (d, $J$ = 9.0 Hz, 1 H), 7.00 - 6.93 (m, 2 H), 6.65 (dd, $J$ = 2.4, 9.0 Hz, 1 H), 6.47 (d, $J$ = 2.2 Hz, 1 H), 3.87 (s, 3 H), 3.48 (q, $J$ = 7.1 Hz, 4 H), 1.25 (t, $J$ = 7.1 Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 192.7, 192.3, 164.3, 160.4, 159.3, 153.9, 148.4, 132.6, 131.9, 126.1, 114.2, 113.1, 110.3, 108.5, 97.1, 55.6, 45.4, 12.5. HRMS (ESI) calcd. for C$_{22}$H$_{21}$NO$_5$ (M+H)$^+$: 380.1492, found: 380.1496.
1-(2-oxo-2\textit{H}-chromen-3-yl)-2-(4-(trifluoromethyl)phenyl)ethane-1,2-dione (2aa)

Yellow solid (22.9 mg, 31%), mp. 218.3 - 219.4 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.51 (s, 1 H), 8.01 - 7.93 (m, 2 H), 7.46 (d, $J = 9.0$ Hz, 1 H), 7.20 - 7.12 (m, 2 H), 6.66 (dd, $J = 2.4$, 9.0 Hz, 1 H), 6.47 (d, $J = 2.3$ Hz, 1 H), 3.49 (q, $J = 7.1$ Hz, 4 H), 1.26 (t, $J = 7.2$ Hz, 6 H).$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 192.3, 191.9, 166.2 (d, $J = 256.0$ Hz), 160.6, 159.4, 154.0, 148.3, 132.7 (d, $J = 9.54$ Hz), 129.5 (d, $J = 2.93$ Hz), 116.05 (d, $J = 22.0$ Hz), 112.8, 110.4, 108.6, 97.2, 45.4, 12.5. $^{19}$F NMR (376.5 MHz, CDCl$_3$): $\delta$ -103.4. HRMS (ESI) calcd. for C$_{21}$H$_{18}$FNO$_4$ (M+Na)$^+$: 390.1112, found: 390.1113.

1-(7-(diethylamino)-2-oxo-2\textit{H}-chromen-3-yl)-2-(4-(trifluoromethyl)phenyl)ethane-1,2-dione (2ab)

Yellow solid (28.1 mg, 34%), mp. 191.5 - 193.7 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.53 (s, 1 H), 8.07 - 8.02 (m, $J = 8.1$ Hz, 2 H), 7.77 - 7.73 (m, $J = 8.2$ Hz, 2 H), 7.48 (d, $J = 9.0$ Hz, 1 H), 6.68 (dd, $J = 2.4$, 9.0 Hz, 1 H), 6.48 (d, $J = 2.3$ Hz, 1 H), 3.49 (q, $J = 7.1$ Hz, 4 H), 1.27 (t, $J = 7.2$ Hz, 6 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 192.8, 191.5, 160.9, 159.4, 154.2, 148.3, 135.8, 134.9 (q, $J = 33.0$ Hz ), 132.9, 129.7, 125.8 (q, $J = 3.7$ Hz ), 123.6 (q, $J = 272.9$ Hz), 112.5, 110.6, 108.7, 97.2, 45.4, 12.5. $^{19}$F NMR (376.5 MHz, CDCl$_3$): $\delta$ -63.2. HRMS (ESI) calcd. for C$_{22}$H$_{18}$F$_3$NO$_4$ (M+H)$^+$: 418.1261, found: 418.1261.
9. NMR spectra of all compounds

**Figure S17.** $^1$H NMR spectrum of compound 1p

**Figure S18.** $^{13}$C NMR spectrum of compound 1p
Figure S19. $^{19}$F NMR spectrum of compound 1p

Figure S20. $^1$H NMR spectrum of compound 1q
**Figure S21.** $^{13}$C NMR spectrum of compound 1q

**Figure S22.** $^1$H NMR spectrum of compound 1r
Figure S23. $^{13}$CNMR spectrum of compound 1r

Figure S24. $^1$H NMR spectrum of compound 1s
Figure S25. $^{13}$C NMR spectrum of compound 1s

Figure S26. $^1$H NMR spectrum of compound 1t
Figure S27. $^{13}$C NMR spectrum of compound 1t

Figure S28. $^1$H NMR spectrum of compound 1u
Figure S29. $^{13}$C NMR spectrum of compound 1u

Figure S30. $^1$H NMR spectrum of compound 1v
Figure S31. $^{13}$C NMR spectrum of compound 1v

Figure S32. $^{19}$F NMR spectrum of compound 1v
Figure S33. $^1$H NMR spectrum of compound 1w

Figure S34. $^{13}$C NMR spectrum of compound 1w
Figure S35. $^1$H NMR spectrum of compound 1x

Figure S36. $^{13}$C NMR spectrum of compound 1x
Figure S37. $^{19}$F NMR spectrum of compound 1x

Figure S38. $^1$H NMR spectrum of compound 1y
Figure S39. $^{13}$C NMR spectrum of compound 1y

Figure S40. $^1$H NMR spectrum of compound 1z
Figure S41. $^{13}$C NMR spectrum of compound 1z

Figure S42. $^1$H NMR spectrum of compound 1aa
**Figure S43.** $^{13}$C NMR spectrum of compound 1aa

**Figure S44.** $^1$H NMR spectrum of compound 1aa
Figure S45. $^1$H NMR spectrum of compound 1ab

Figure S46. $^{13}$C NMR spectrum of compound 1ab
Figure S47. $^{19}$F NMR spectrum of compound 1ab

Figure S48. $^1$H NMR spectrum of compound 2a
Figure S49. $^{13}$C NMR spectrum of compound 2a

Figure S50. $^1$H NMR spectrum of compound 2b
Figure S51. $^{13}$C NMR spectrum of compound 2b

Figure S52. $^1$H NMR spectrum of compound 2c
Figure S53. $^{13}$C NMR spectrum of compound 2e

Figure S54. $^1$H NMR spectrum of compound 2d
Figure S55. $^{13}$C NMR spectrum of compound 2d

Figure S56. $^{19}$F NMR spectrum of compound 2d
Figure S57. $^1$H NMR spectrum of compound 2e

Figure S58. $^{13}$C NMR spectrum of compound 2e
Figure S59. $^1$H NMR spectrum of compound 2f

Figure S60. $^{13}$C NMR spectrum of compound 2f
Figure S61. $^{19}$F NMR spectrum of compound 2f

Figure S62. $^1$H NMR spectrum of compound 2g
Figure S63. $^{13}$C NMR spectrum of compound 2g

Figure S64. $^1$H NMR spectrum of compound 2h
Figure S65. $^{13}$C NMR spectrum of compound 2h

Figure S66. $^1$H NMR spectrum of compound 2i
Figure S67. $^{13}$C NMR spectrum of compound 2i

Figure S68. $^1$H NMR spectrum of compound 2j
Figure S69. $^{13}$C NMR spectrum of compound 2j

Figure S70. $^{19}$F NMR spectrum of compound 2j
Figure S71. $^1$H NMR spectrum of compound 21

Figure S72. $^{13}$C NMR spectrum of compound 21
Figure S73. $^1$H NMR spectrum of compound 2m

Figure S74. $^{13}$C NMR spectrum of compound 2m
Figure S75. $^{19}$F NMR spectrum of compound 2m

Figure S76. $^1$H NMR spectrum of compound 2n
Figure S77. $^{13}$C NMR spectrum of compound 2n

Figure S78. $^1$H NMR spectrum of compound 2o
Figure S79. $^{13}$C NMR spectrum of compound 2o

Figure S80. $^{19}$F NMR spectrum of compound 2o
Figure S81. $^1$H NMR spectrum of compound 2p

Figure S82. $^{13}$C NMR spectrum of compound 2p
Figure S83. $^{19}$F NMR spectrum of compound 2p

Figure S84. $^1$H NMR spectrum of compound 2q
Figure S85. $^{13}$C NMR spectrum of compound 2q

Figure S86. $^1$H NMR spectrum of compound 2r
Figure S87. $^{13}$C NMR spectrum of compound 2r

Figure S88. $^1$H NMR spectrum of compound 2s
Figure S89. $^{13}$C NMR spectrum of compound 2s

Figure S90. $^1$H NMR spectrum of compound 2t
Figure S91. $^{13}$C NMR spectrum of compound 2t

Figure S92. $^1$H NMR spectrum of compound 2u
Figure S93. $^{13}$C NMR spectrum of compound 2u

Figure S94. $^1$H NMR spectrum of compound 2v
**Figure S95.** $^{13}$C NMR spectrum of compound 2v

**Figure S96.** $^{19}$F NMR spectrum of compound 2v
Figure S97. $^1$H NMR spectrum of compound 2w

Figure S98. $^{13}$C NMR spectrum of compound 2w
Figure S99. $^1$H NMR spectrum of compound 2x

Figure S100. $^{13}$C NMR spectrum of compound 2x
Figure S101. $^{19}$F NMR spectrum of compound 2x

Figure S102. $^1$H NMR spectrum of compound 2y
Figure S103. $^{13}$C NMR spectrum of compound $2y$

Figure S104. $^1$H NMR spectrum of compound $2z$
Figure S105. $^{13}$C NMR spectrum of compound 2z

Figure S106. $^1$H NMR spectrum of compound 2aa
Figure S107. $^{13}$C NMR spectrum of compound 2aa

Figure S108. $^{19}$F NMR spectrum of compound 2aa
Figure S109. $^1$H NMR spectrum of compound 2ab

Figure S110. $^{13}$C NMR spectrum of compound 2ab
Figure S111. $^{19}$F NMR spectrum of compound 2ab
10. X-ray crystallographic data

1) Structure determination of 2a

The structure of 2a was determined by the X-ray diffraction. Recrystallized from EtOH/dichloromethane (v/v = 1/1). Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2036909.

Table S2 Crystal data and structure refinement for 2a.

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2) Structure determination of 2g

The structure of 2g was determined by the X-ray diffraction. Recrystallized from EtOH/dichloromethane (v/v = 1/1). Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2026429.

Table S3 Crystal data and structure refinement for 2g.

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Table S3 Crystal data and structure refinement for 2g.
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c/Å 14.7714(7)
α/° 90
β/° 94.995(4)
γ/° 90
Volume/Å³ 1992.74(15)
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ρ calc g/cm³ 1.275
μ/mm⁻¹ 0.698
F(000) 800.0
Crystal size/mm³ 0.22 × 0.15 × 0.1
Radiation CuKα (λ = 1.54184)
2Θ range for data collection/° 8.178 to 134.16
Index ranges -17 ≤ h ≤ 16, -8 ≤ k ≤ 11, -17 ≤ l ≤ 16
Reflections collected 7221
Independent reflections 3554 [Rint = 0.0250, Rsigma = 0.0343]
Data/restraints/parameters 3554/0/264
Goodness-of-fit on F² 1.028
Final R indexes [I>=2σ (I)] R₁ = 0.0477, wR₂ = 0.1199
Final R indexes [all data] R₁ = 0.0667, wR₂ = 0.1383
Largest diff. peak/hole / e Å⁻³ 0.13/-0.17

3) Structure determination of 2s

The structure of 2s was determined by the X-ray diffraction. Recrystallized from EtOH/dichloromethane (v/v= 1/1). Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2036910.
Table S4 rystal data and structure refinement for 2s.

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